

An Electrochemical Impedance Spectroscopy Study of Methanol Oxidation on Smooth Pt

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INTRODUCTION

In recent years increasing attention has been devoted to the oxidation of small organic molecules due to their potential use in fuel cells. The use of methanol as a fuel, particularly, has attracted much interest because it is widely available and can be stored, handled and distributed to the consumer easily. However, there are some problems that limit the efficiency of a direct methanol fuel cell. These are intimately related to the reaction mechanism, which involves the production of poisoning intermediates, leading to an inhibition of the reaction. The mechanism of methanol oxidation has been extensively studied with in situ spectroscopic techniques and mass spectrometry. Electrochemical techniques, such as voltammetry and chronoamperometry have been mostly used in a qualitative way to compare electrode materials or solution compositions. Studies involving impedance spectroscopy have been done to examine the behavior of operational systems, in an attempt to achieve new criteria for the comparison of cells working with different components and configurations [1,2]. On the other hand, fundamental research using impedance measurements to obtain information about the mechanism of the oxidation of methanol, or related molecules, on noble metals are not usual. Results for the oxidation of formic acid have been discussed in terms of an equivalent circuit but the frequency range was severely limited[3]. In a short communication, the investigation of the oxidation of methanol with impedance measurements was briefly analysed in a qualitative way[4]. In the present work, some aspects of the mechanism of methanol oxidation are discussed on the basis of chronoamperometric and impedance experiments.

EXPERIMENTAL

Experiments were carried out in a three-electrode electrochemical cell with a platinum counter electrode and a reversible hydrogen electrode as reference. The working electrode consisted of a polycrystalline Pt wire (Degussa S.A.) of 6.5mm in diameter. The base electrolyte was 0.5M H₂SO₄ prepared with water from a Milli-Pore/Milli-Q system and Merck "suprapur" reagents. The solution was 1M methanol in the base electrolyte. The electronic set-up consisted of a 1286 Electrochemical Interface and a 1250 FRA Solartron Schlumberger, a Nicolet 430 oscilloscope, a and a Kemo variable filter. This system was connected to a personal computer. The impedance experiments were performed at different potentials in the range 600 to 900mV. A potential step was applied from 50mV up to the working potential and the impedance response was recorded at different times.

RESULTS AND DISCUSSION

A polarization curve was first constructed for methanol oxidation on Pt using the current values obtained from chronoamperometric curves recorded at several potentials in the range 600mV to 900 mV vs RHE. The plot shows a

peak at about 800 mV. Even for very long waiting times of the order of 40 hours, it was not possible to obtain a true steady state current. This is probably related to the increasing coverage of the electrode surface by strongly adsorbed intermediates, leading to a continuous decrease of the current[5].

During the chronoamperometric experiments, impedance spectra were obtained at different times in the frequency range from 10kHz to either 5mHz or 1mHz depending on the DC current stability. The impedance plots on the complex plane were characterized by a distorted semi-circle and a loop at low potentials.

Impedance spectra taken at different times at potentials in the rising part of the polarization curve show the same qualitative aspect but there's an increase in the radius of the semi-circle. This may be explained in terms of an increase in the double layer capacity because of the continuous poisoning of the surface by residues from the partial dehydrogenation of methanol as shown by FTIR and thermal desorption experiments[6].

An inductive loop at low frequencies is observed for potentials in the region of methanol oxidation. This is usually related to adsorption processes and in this case it is presumably caused by the adsorption of methanol. Impedance measurements on a direct methanol fuel cell with a Pt-Ru anode have shown a similar inductive loop that was interpreted in terms of the adsorption of methanol[2]. The results are comparable because, at room temperature the adsorption of methanol occurs only on Pt sites [7].

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